Photocapacitive detection of hole emission from DX center in n-type Al0.3Ga0.7As doped with Te

doi: 10.1063/1.371848

Photocapacitive detection of hole emission from *DX* center in *n*-type $Al_{0.3}Ga_{0.7}As$ doped with Te

Akihiko Murai
Telecommunications Advancement Organization of Japan SENDAI Research Center, 19 Koeji Aza Nagamachi Aoba, Sendai 980-0868, Japan

Yutaka Oyama
Department of Material Science and Engineering, Graduate School of Engineering, Tohoku University, 02 Aoba Aza Aramaki Aoba, Sendai 980-0845, Japan

Jun-ichi Nishizawa[a)]
Semiconductor Research Institute of Semiconductor Research Foundation, Kawauchi Aoba, Sendai 980-0862, Japan

(Received 3 May 1999; accepted for publication 20 September 1999)

Photocapacitance (PHCAP) measurements are applied to liquid-phase epitaxially grown *n*-$Al_{0.3}Ga_{0.7}As$ crystals at different temperatures. The PHCAP measurements revealed deep levels optically located at 0.5 eV below the conduction band and 1.5 eV above the valence band [$E_c-0.5$ eV level (Te-related *DX* center) and $E_v+1.5$ eV level]. The thermal activation energy of electron capture at the ionized $E_c-0.5$ eV level was found to be 31 meV. The optical hole emission process from the $E_v+1.5$ eV level was enhanced with increasing sample temperature. After 1.5 eV monochromatic light preirradiation, the $E_c-0.5$ eV level was detected in an intentionallly undoped *n*-$Al_{0.3}Ga_{0.7}As$ sample. From these results, the structure of the Te-related *DX* center is discussed. © *2000 American Institute of Physics.* [S0021-8979(00)02301-X]

I. INTRODUCTION

Deep donor levels which are often called *DX* centers have been observed in many compound semiconductors. Persistent photoconductivity (PPC) effects, attributed to the *DX* level, were reported in nonstoichiometric CdTe (1964),[1] and $GaAs_{1-x}P_x$ (1968).[2] In $Al_xGa_{1-x}As$ ternary alloy systems, the *DX* centers have been greatly concerned with the effect of deviation on the electrical characteristics of $Al_xGa_{1-x}As$-based devices such as the high electron mobility transistor, etc. In view of the defect structure, many investigations have also been reported to explain the large difference between thermal and optical activation energy. Many models have been proposed for the atomic structure of the *DX* center.[2–8] In 1977, Nishizawa *et al.* reported that the photocapacitance (PHCAP) measurements revealed the major deep centers at ~0.65 eV below the conduction band in *p*-$Al_{0.3}Ga_{0.7}As$/*n*-$Al_{0.65}Ga_{0.35}As$ heterojunction diodes fabricated with the liquid-phase epitaxy (LPE) of temperature difference method (TDM),[9–11] which exhibited PPC effects at low temperature[12] and the nonstoichiometric defect-donor complex model was proposed as an explanation. Later, this level was called the *DX* center in $Al_xGa_{1-x}As$.[3] It has been reported that the so-called *DX* center is formed in *n*-type $Al_xGa_{1-x}As$ with an Al composition $x>0.22$, and that the density of the *DX* center is nearly equal to the donor concentration. In conjunction with other results, it has been proposed that the origin of the *DX* center is the donor impurity itself.[13] Recently, we have reported the effects of arsenic vapor pressure on the formation of dominant deep levels detected in *n*-$Al_{0.3}Ga_{0.7}As$.[14] Te-doped $Al_{0.3}Ga_{0.7}As$ crystals grown by LPE were annealed at 900 °C for 1 h under controlled arsenic vapor pressure (CVP), and PHCAP measurements, Hall effect measurements, and photoluminescence measurements were carried out. From these experimental results, we have proposed that in $Al_xGa_{1-x}As$:Te ternary alloy systems, the dominant deep levels, i.e., the *DX* centers are affected by the stoichiometric composition of the crystals, and that these deep levels are associated with at least the donor impurity Te and the excess arsenic composition. The PHCAP measurements revealed two types of deep levels, the optical activation energy of which are 0.5 and 1.1 eV, respectively, ($E_c-0.5$ eV level and $E_c-1.1$ eV level).[15] The $E_c-1.1$ eV level density decreased with increasing Te concentration in solution during crystal growth. In conjunction with other experimental results, we have proposed that the $E_c-1.1$ eV level interacts with $E_c-0.5$ eV level.

Up to now, some reports have been published on the relation of the *DX* center and minority carrier, i.e., hole. But, hole emission phenomena have not been reported yet. In this article, the PHCAP measurements have been applied to LPE-grown Te-doped *n*-$Al_{0.3}Ga_{0.7}As$. The PHCAP measurements were performed with changing measurement temperature. The phenomenon of optical hole emission process concerning the deep levels (Te related *DX* center) is shown.

II. EXPERIMENT

A. Sample preparation

Te-doped $Al_xGa_{1-x}As$ ($x=0.33\pm0.02$) layers were epitaxially grown with the LPE of the TDM under CVP.[11,16] The substrates used for the PHCAP measurements were Si

[a)]Electronic mail: nisizawa@hanken-sri.or.jp

doped n^+-GaAs crystals (carrier concentration $n=2\times10^{18}$ cm^{-3}) prepared with the horizontal Bridgman method. The crystallographic orientation of the substrate was {100}. The growth time was 60 min. The arsenic vapor pressure applied during crystal growth was fixed at 0.9 Torr in the present experiments. The average thickness of the epitaxial layer obtained was ~1 μm. In order to make metal/semiconductor diodes, Au was evaporated onto a sample surface after AuGe/Au was alloyed on the back at 450 °C for 1 min to provide an ohmic contact.

B. PHCAP measurement

The PHCAP method has many advantages over other thermal excitation methods such as the deep level transient spectroscopy (DLTS) method, because of its optical excitation at a constant low temperature. PHCAP measurements were carried out under constant voltage conditions at each setting temperature. The sample diode was cooled in the dark by applying the forward bias voltage from room temperature to measuring temperature. Then, a constant reverse bias voltage (−0.500 V) was applied and monochromatic light fed from a monochometer was irradiated from the long wave length into the depletion region of the sample diode. The junction capacitance was measured by using a capacitance meter. The measuring signal amplitude and frequency used in the present experiments were 15 mV and 100 kHz, respectively. The ionized level density was determined as

$$\Delta N_t=(V_{\mathrm{dep}}-V_{\mathrm{appl}})\left(\frac{2}{\epsilon q}\right)(C_{\mathrm{ph}}^2-C_{\mathrm{dark}}^2), \tag{1}$$

where ΔN_t is the ionized level density, V_{dep} is the diffusion potential, V_{appl} is the applied voltage, C_{ph} and C_{dark} are the measured capacitances per unit area under monochromatic light irradiation and the dark condition, respectively, ϵ is the dielectric constant, and q is the elementary electric charge. Precise description of the PHCAP measurements has been reported in Refs. 17–19.

III. RESULTS AND DISCUSSION

Figures 1(a) and (b) show the PHCAP spectra of Te-doped n-$Al_{0.3}Ga_{0.7}As$ grown from the AlGaAs solution with 4.7×10^{-3} wt % Te concentration. The PHCAP measurements were carried out at (a) 40 and (b) 85 K. Before each monochromatic light irradiation, the sample was forward biased to neutralize each of the photoionized deep levels. In Figs. 1(a) and 1(b), the increase in the ionized level density is caused by the photoionization of the occupied deep levels, and the decrease of ionized level density is caused by the occupation of electrons at deep levels. Figure 1(a) shows that the dominant deep levels are detected at 0.5 eV below the conduction band ($E_c-0.5$ eV). From Fig. 1(a), it is considered that once the $E_c-0.5$ eV level is photoionized, this level hardly captures an electron at 40 K. This characteristic is the same with the so-called *DX* center. In Fig. 1(b), in which the sample temperature is 85 K, in conjunction with $E_c-0.5$ eV level, it is noticed that there is a decrease of signal when 1.5 eV monochromatic light is irradiated to the sample. As concerns this signal, two types of optical transition process are considered. One type is the optical hole emission process to the valence band, and the other type is the optical electron transition process from the conduction band to the deep level. In our experimental conditions, the measurement region is considered as the depletion layer of AlGaAs crystals, in which there are few electrons. So, it is considered that the optical hole emission process mainly occurs, and deep levels are detected at 1.5 eV above the valence band. It is shown that some parts of $E_c-0.5$ eV can be neutralized by forward biasing at 85 K. In Fig. 1(b), the ionized level density is smaller than the density shown in Fig. 1(a). It is considered that at 85 K, the $E_c-0.5$ eV level is thermally ionized in part. Figure 1(c) shows the tempera-

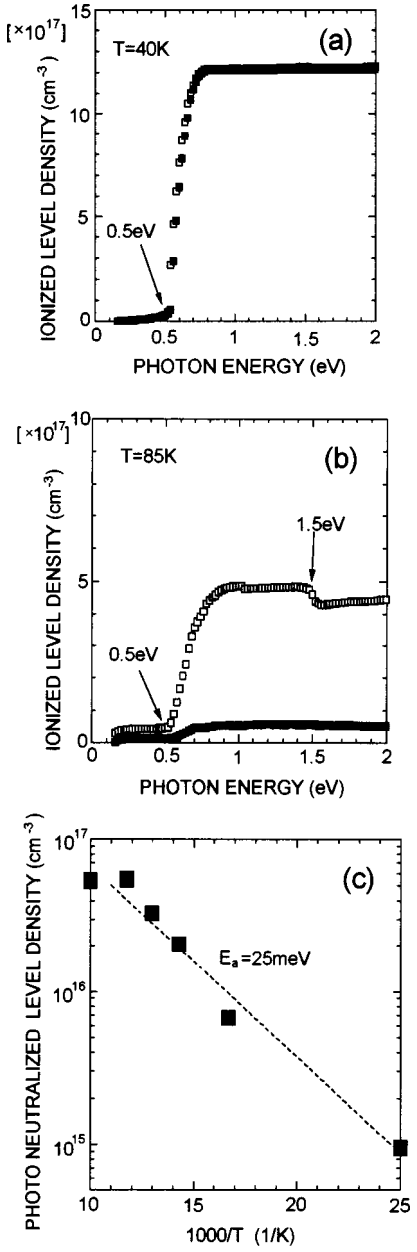

FIG. 1. (a) and (b) Typical ion density PHCAP spectra of $Al_{0.3}Ga_{0.7}As$ at (a) 40 and (b) 85 K. (a) and (b) represent the ion density in the dark (■) after neutralization process of deep level and the photoionized level density (□), respectively. (c) Relation between temperature and photoneutralized level ($E_v+1.5$ eV level) density.

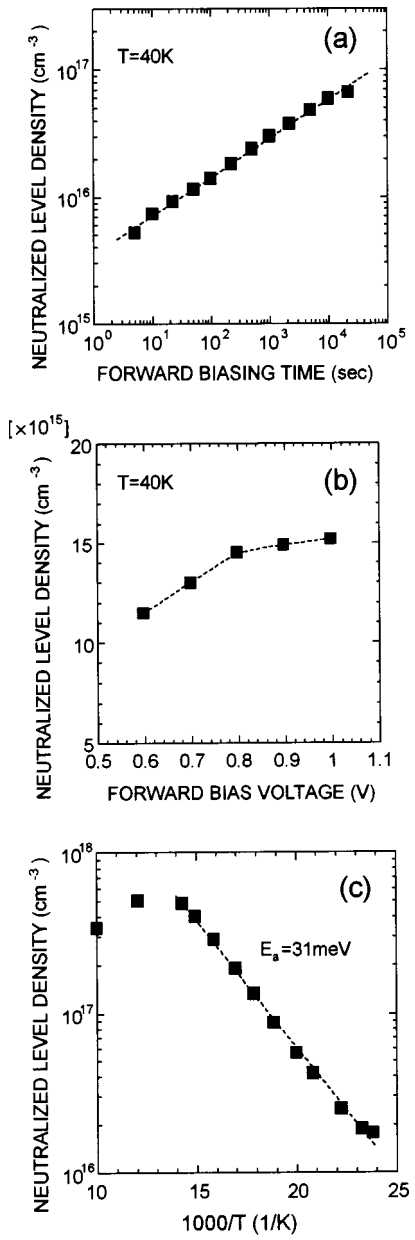

FIG. 2. (a) Forward biasing (0.9 V) time dependencies of the neutralized $E_c-0.5$ eV level density at 40 K. (b) Forward bias voltage dependencies of the neutralized $E_c-0.5$ eV level density at 40 K, at which forward biasing time is 120 s. (c) Temperature dependencies of neutralized $E_c-0.5$ eV level density.

ture dependencies of the optically neutralized level ($E_v+1.5$ eV level) density. It is shown that detected $E_v+1.5$ eV level density increases with increasing sample temperature.

Figure 2(a) shows the forward biasing time dependencies of the neutralized $E_c-0.5$ eV level density at 40 K. For this measurement, the sample was irradiated with 1.0 eV monochromatic light to photoionize the $E_c-0.5$ eV level, and then forward bias voltage (+0.9 V) was supplied for predetermined constant times. After that, the neutralized $E_c-0.5$ eV level density was determined as follows:

$$\Delta N_{\text{neut}}=(V_{\text{dep}}-V_{\text{appl}})\left(\frac{2}{\epsilon q}\right)(C^2_{\text{ph(1.0 eV)}}-C^2_{\text{dark}}), \qquad (2)$$

where ΔN_{neut} is neutralized $E_c-0.5$ eV level density by the electron capture from the conduction band and $C_{\text{ph(1.0 eV)}}$ is the measured capacitance per unit area under 1.0 eV monochromatic light irradiation. It is shown that the neutralized level density increases as forward biasing time increases. From this experimental result, seven years seem to be needed to neutralize all the photoionized $E_c-0.5$ eV levels at 40 K. Figure 2(b) shows the forward bias voltage dependencies of the neutralized $E_c-0.5$ eV level density at 40 K. For this measurement, forward biasing time was kept to 120 s. It is shown that the neutralized level density increases as forward bias voltage increases and then saturates to $\sim 1.5\times 10^{16}$ cm^{-3}. Figure 2(c) shows the temperature dependencies of the neutralized $E_c-0.5$ eV level density caused by forward biasing. The measurement was performed as follows, (1) the sample is cooled to 40 K, (2) 1.0 eV monochromatic light is irradiated and asymptotic capacitance [$C_{\text{ph(1.0 eV)}}$] is measured in the condition of reverse biasing (−0.5 V), (3) the temperature is changed to setting value with reverse biasing (−0.5 V), (4) forward bias voltage (+0.6 V) is applied for 120 s at the setting temperature, after that, (5) capacitance in the dark (C_{dark}) is measured in the condition of reverse biasing (−0.5 V). This experiment sequence was performed at each setting temperature. It is shown that the neutralized level density increases with increasing measurement temperature, but decreases at higher temperatures more than 80 K. At the higher temperature region, the influence of thermal electron emission from the $E_c-0.5$ eV level is considered to increase. From this PHCAP experiment, the thermal activation energy for the electron capture at the ionized $E_c-0.5$ eV level was determined to be 31 meV. These results indicate that the $E_c-0.5$ eV level is considered to have an energy barrier (31 meV) to the electron capture from the conduction band and that the thermal ionization energy is far less than the photoionization energy (0.5 eV), which is a characteristic of the so-called *DX* center. These characteristics are considered to be caused by large lattice relaxation (LLR).[5] Concerning the Te-related *DX* center, the reported value of activation energy of the electron capture rate is 0.18 eV which was obtained by the temperature dependence of the electron concentration.[20] They measured Te-doped $Al_{0.4}Ga_{0.6}As$ ($N_D-N_A=10^{17}-10^{18}$ cm^{-3}). However, a smaller value was obtained in our present experimental conditions. In conjunction with the difference of measurements, there seems to be dependencies of Al composition and donor concentration.

Figure 3 shows the PHCAP spectra of intentionally undoped n-$Al_{0.3}Ga_{0.7}As$. After cooling in the dark with forward bias voltage from room temperature to 77 K, a constant reverse bias voltage was applied and (a) no light, (b) 1.0 eV monochromatic light, and (c) 1.5 eV monochromatic light was preirradiated to the sample. Then, monochromatic light was irradiated from long wavelength. Concerning the deep level detected at 0.5 eV below the conduction band ($E_c-0.5$ eV level) which is considered as the residual Te-related *DX* center, it is not detected in Fig. 3(b) in which 1.0 eV monochromatic light was irradiated before PHCAP measurement, but detected in Figs. 3(a) and 3(c), in which (a) no light and (c) 1.5 eV monochromatic light was preirradiated before PHCAP measurement. It is noticed that the signal

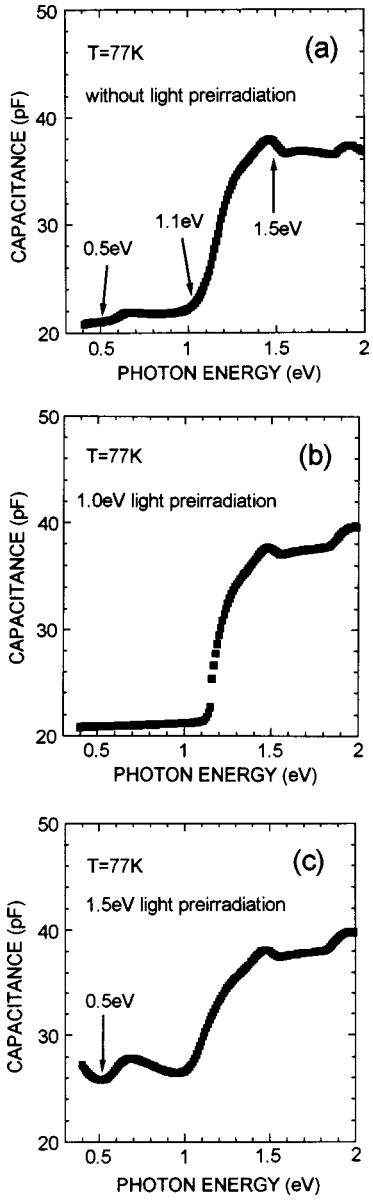

FIG. 3. The PHCAP spectra of intentionally undoped n-$Al_{0.3}Ga_{0.7}As$ at 77 K. After cooling in the dark, (a) no light, (b) 1.0 eV light, and (c) 1.5 eV light was preirradiated to the sample.

response concerning the $E_c-0.5$ eV level in Fig. 3(c) is larger than that in Fig. 3(a). Concerning the optically ionized deep level at 1.1 eV below the conduction band ($E_c-1.1$ eV level) shown in Figs. 3(a), 3(b), and 3(c), we have reported and proposed that the $E_c-1.1$ eV level is affected by the stoichiometric composition of the crystals and interacts with the $E_c-0.5$ eV level.[15]

Some reports have been published on the relation of the *DX* center and minority carrier (hole). It has been reported that the near-band gap photoluminescence of AlGaAs:Si shows a slow intensity transient after cooling the sample in darkness to low temperatures.[21] By investigating the behavior for below- and above-band gap illumination, they explained this transient by the concept of hole capture at the *DX* center (hole-capture cross section $\sigma_{DX,h} \geqslant 2 \times 10^{-16}$ cm^2).

Current instabilities in Schottky diodes prepared on Si-doped AlGaAs have been reported.[22] It has been shown that at low temperature hole injection under forward bias causes a dramatic increase in the concentration of positively charged donors, which can be detected through capacitance–voltage profiling. This phenomenon has been ascribed to direct hole capture at the *DX* center following electron-hole radiative recombination.

With respect to DLTS, positive DLTS signals are reported in Schottky diodes made on Te-doped AlGaSb when forward-bias filling pulses are used.[23] They discussed these observations in terms of minority carrier (hole) injection and subsequent capture by the *DX* centers. They expected that electron capture from the conduction band is more predominant than hole emission into the valence band since the thermal energy barrier for electron capture is much smaller than the thermal energy barrier for hole emission.

From the results shown in Fig. 1, it is considered that there are at least two types of optical transition processes in Te-doped $Al_{0.3}Ga_{0.7}As$ when monochromatic light, whose photon energy is less than the band gap photon energy, is irradiated to the sample. One type is optical electron emission from the deep level ($E_c-0.5$ eV level), and the threshold photon energy is 0.5 eV. Once the $E_c-0.5$ eV level is photoionized at low temperature, it is difficult to neutralize this level by electron injection as shown in Fig. 2. We obtained the activation energy for neutralizing this level by the use of the PHCAP method mentioned before. This barrier causes PPC which is a well-known characteristic of the *DX* center in AlGaAs.[24,25] The other type is the optical hole emission from the deep level ($E_v+1.5$ eV level) to the valence band, and the threshold photon energy is 1.5 eV. It is considered that these two types of optical transition process both occur when monochromatic light with larger photon energy than 1.5 eV is irradiated to the sample. From Fig. 1(c), it is considered that there seems to be activation energy to cause this optical hole emission process. In Fig. 3, we reported the three types of PHCAP spectra with different monochromatic light preirradiations to the sample, at which the $E_c-0.5$ eV level was clearly detected with the condition of 1.5 eV monochromatic light preirradiation. These experimental results can be understood by considering that an electron transfers to the $E_c-0.5$ eV level from the valence band because of the 1.5 eV light irradiation. So, it is considered that the $E_c-0.5$ eV level and $E_v+1.5$ eV level are the same level, i.e., we observed optical electron emission and optical hole emission from the same Te-related *DX* center. The band gap energy of $Al_xGa_{1-x}As$ ($x=0.33$) at 77 K is 1.92 eV. The total of 0.5 and 1.5 eV is not the same as the band gap. This energy difference is considered to be understood by the energy shift caused by lattice relaxation. From the result of Fig. 1(c), it is considered that there is a thermal energy barrier to cause optical hole emission from the Te-related *DX* center. One possibility is that this hole emission process is caused by a lattice relaxation combination of the valence band and *DX* center.

The so-called *DX* centers observed in donor-doped AlGaAs have been intensively studied, but the fine structures of these centers are less certain. In the negative-*U* model of the *DX* centers,[4] it was suggested they are characterized by

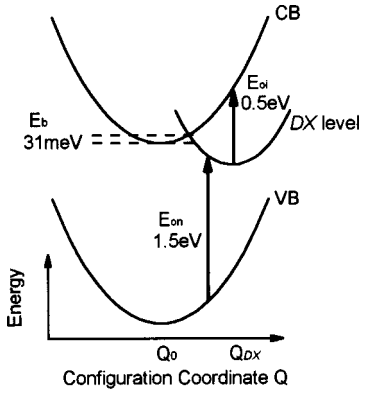

FIG. 4. Configuration-coordinate diagram of the Te-related *DX* center.

two types of donor states. One is directly related to a substitutional shallow effective-mass state, another is a deep localized state known as the *DX* center. In the latter, the substitutional donor and its neighbor atoms largely relax from their lattice positions and the energy level becomes deeper when the donor traps two electrons. By this model, there cannot be a deep *DX* center level before trapping two electrons by the donor. Whereas more detailed investigations of AlGaAs are necessary, we propose that the dominant deep levels in Te-doped n-$Al_{0.3}Ga_{0.7}As$, i.e., the *DX* center remains at a deep level before capturing an electron, and the optical energy level position is 0.5 eV below the conduction band and 1.5 eV above the valence band. There is an energy barrier to optical hole emission from the *DX* center from our present experimental results. In conjunction with our other reports,[14,15] this proposal leads to the idea that the *DX* center seems to be a stoichiometry dependent complex defect rather than a simple substitutional donor. But this proposal is not consistent with the negative-*U* model.

In summary, the LLR model proposed by our experimental results for the properties of the Te-related *DX* center in $Al_{0.3}Ga_{0.7}As$ is shown by the configuration-coordinate diagram in Fig. 4, in which E_b is thermal capture energy, E_{oi} and E_{on} are optical ionization energy and optical neutralization energy, respectively.

IV. CONCLUSION

The optical hole emission processes in Te-doped $Al_xGa_{1-x}As$ ($x=0.33$) crystals grown by LPE were measured with the PHCAP method at different temperatures. The PHCAP measurements revealed deep levels optically located at 0.5 eV below the conduction band ($E_c-0.5$ eV) and 1.5 eV above the valence band ($E_v+1.5$ eV). The thermal activation energy of electron capture to the photoionized $E_c-0.5$ eV level was estimated to be 31 meV from PHCAP methods. The optical hole emission process from the $E_v+1.5$ eV level was enhanced with increasing sample temperature. After 1.5 eV monochromatic light preirradiation, the $E_c-0.5$ eV level was clearly detected in intentionally undoped n-$Al_{0.3}Ga_{0.7}As$. From these results, it is considered that in AlGaAs:Te ternary alloy systems, the $E_c-0.5$ eV level and the $E_v+1.5$ eV level are the same level, and the Te-related *DX* center remains at a deep level even before capturing an electron. From this consideration, it seems that the Te-related *DX* center is a stoichiometry dependent complex defect rather than a simple substitutional donor.

[1] M. R. Lorenz, B. Segall, and H. M. Woodbury, Phys. Rev. **134**, A751 (1964).
[2] M. G. Craford, G. E. Stillman, J. A. Rossi, and N. Holonyak, Phys. Rev. **168**, 867 (1968).
[3] D. V. Lang, R. A. Rogan, and M. Jaros, Phys. Rev. B **19**, 1015 (1979).
[4] D. J. Chadi and K. J. Chang, Phys. Rev. B **39**, 10063 (1989).
[5] P. M. Mooney, J. Appl. Phys. **67**, R1 (1990).
[6] J. E. Dmochowski, L. Dobaczewski, J. M. Langer, and W. Jantsch, Phys. Rev. B **40**, 9671 (1989).
[7] B. H. Cheong and K. J. Chang, Phys. Rev. B **46**, 13131 (1992).
[8] H. H. Zhan, J. Y. Kang, Z. Y. Wu, and Q. S. Huang, J. Appl. Phys. **84**, 2497 (1998).
[9] J. Nishizawa, S. Shinozaki, and K. Ishida, J. Appl. Phys. **44**, 1638 (1973).
[10] J. Nishizawa and Y. Okuno, IEEE Trans. Electron Devices **ED–22**, 716 (1975).
[11] J. Nishizawa, Y. Okuno, and H. Yadano, J. Cryst. Growth **31**, 215 (1975).
[12] J. Nishizawa, K. Suto, and T. Teshima, J. Appl. Phys. **48**, 3484 (1977).
[13] M. Mizuta, M. Tachikawa, T. Teshima, and H. Kukimoto, Jpn. J. Appl. Phys., Part 1 **24**, L143 (1985).
[14] A. Murai, J. Nishizawa, Y. Oyama, K. Suto, and N. Chubachi, J. Appl. Phys. **79**, 3930 (1996).
[15] J. Nishizawa, A. Murai, Y. Oyama, and K. Suto, J. Electrochem. Soc. **145**, 2905 (1998).
[16] J. Nishizawa, Y. Okuno, and K. Suto, *JARECT 19, Semiconductor Technology*, edited by J. Nishizawa (OHM and North-Holland, Tokyo, 1986).
[17] J. Nishizawa, Y. Oyama, and K. Dezaki, J. Appl. Phys. **67**, 1884 (1990).
[18] Y. Oyama, J. Nishizawa, and K. Dezaki, J. Appl. Phys. **70**, 833 (1991).
[19] J. Nishizawa, Y. Oyama, and K. Dezaki, J. Appl. Phys. **69**, 1446 (1991).
[20] D. V. Lang and R. A. Rogan, Inst. Phys. Conf. Ser. **43**, 433 (1979).
[21] G. Brunthaler, K. Ploog, and W. Jantsch, Phys. Rev. Lett. **63**, 2276 (1989).
[22] R. Mosca, E. Gombia, A. Bosacchi, S. Franchi, C. Ghezzi, and P. Frigeri, J. Appl. Phys. **75**, 5072 (1994).
[23] E. Gombia, R. Mosca, S. Franchi, C. Ghezzi, and R. Magnanini, J. Appl. Phys. **84**, 5337 (1998).
[24] R. J. Nelson, Appl. Phys. Lett. **31**, 351 (1977).
[25] N. Chand, T. Henderson, J. Klem, W. T. Masselink, R. Fisher, Y. C. Chang, and H. Morkoc, Phys. Rev. B **30**, 4481 (1984).